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Growth and characterization of single crystals of ternary chalcogenides for laser applications

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ABSTRACT

Bulk single crystals up to 20 mm in diameter and 40 mm long for LiInS_2 and up to 10 mm, 20 mm, respectively, for LiInSe_2 have been grown. Their color changed from colorless to rose for the first one and from yellow to dark red for the other. All crystals have wurtzite-type lattice (Pna2₁ space group), lattice parameters were determined. A band gap was found to be 3.72 and 3.57 eV for LiInS_2 and 3.02, 2.86 eV for LiInSe_2 at 80 and 300K respectively. Color variations are due to point defects, first of all to interstitial sulfur, resulting in additional wide absorption bands in the shortwave part of transparency range. For LiInS_2 the SHG phase matching conditions were found to be similar for samples of different color and some difference from Boyd's predictions of 1973 was shown: for XY plane $\Delta\phi \sim +3^\circ$ at 2.6 μm and $\Delta\phi \sim -3$ to -5° at 4-5 μm . Nonlinear susceptibility for LiInS_2 was estimated: $d_{\text{eff}}(\text{XY}) \sim 3.4 \text{ pm/V}$ relative to Boyd's value as 10.6 pm/V. A proper illumination gives a photoinduced change of LiInSe_2 color from dark red to yellow as a result of changes in point defects charge state.

Keywords: lithium indium sulfide/selenide, absorption, color, nonlinear susceptibility, band gap, lattice parameters

1. INTRODUCTION

The mid-IR spectral range is of large importance because the overwhelming majority of chemical compounds has specific vibrational/rotational spectra and their detection and identification make it possible to solve various fundamental and applied tasks in molecular spectroscopy, atmospheric sensing, optical metrology, medicine etc.. To date the most widespread techniques to produce the coherent widely tunable radiation with wavelengths up to 20 μm are based on difference frequency generation of two near-IR lasers in infrared nonlinear optical (NLO) crystals and on use of optical parametric oscillators (OPO). Very few good NLO crystals including GaSe and a set of ternary chalcogenides as AgGaS_2 , AgGaSe_2 et al have been recently used for cw optical parametric oscillator¹ but each of them has its own shortcomings. For GaSe it is a problem with mechanical treatment including finishing, while silver ternary chalcogenides have an insufficient nonlinear susceptibility and low thermal conductivity.

An active search for new promising nonlinear crystals is in progress. The Li-containing ternary chalcogenides such as LiInS_2 and LiInSe_2 are considered as promising ones for generation of coherent radiation in the mid-IR region thanks to their transparency in a wide region from the 0.4 μm for LiInS_2 and 0.6 μm for LiInSe_2 to 12 microns in the mid-IR and relatively high nonlinear susceptibility. The latter was estimated using a wedge technique: d_{33} was shown to be about 18 pm/V for LiInS_2 ² which is 1.5 times higher than that for the wide-spread AgGaS_2 . Moreover there are several additional reasons that make the Li-based crystals very attractive for non-linear optics:

1. The Ag-ion replacement by the lighter Li-ion results in an increase in the frequencies of crystal lattice vibrations and of the Debye temperature. It intensifies the U-processes in phonon-phonon interactions and increases the thermal

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conductivity, which in turn, are accompanied by an increase of the optical damage threshold.

2. LiInS_2 and its analogues crystallise in an mm2 space-group, like KTP, and are related to pyro-electrics and maybe ferro-electrics, where a periodic domain structure can be created and quasi-phase-matching operation (QPM) can be realised. This will allow us to considerably widen the spectral range of generated frequencies and to increase the non-linear conversion efficiency.
3. LiInS_2 crystals have the largest energy gap (3.59 eV at 300 K) among NLO crystals used for the mid-IR, which reduces the effect of two-photon absorption when pumping this crystal by the most widely used diode laser or a Nd:YAG laser.
4. The wurtzite type crystal lattice different from a chalcopyrite one of AgGaS_2 , AgGaSe_2 and ZnGeP_2 type allows us to avoid the difference in sign of the thermal expansion coefficients along different and resulting creation of typical stresses and {112} micro-twin defects. Therefore, these crystals are expected to benefit from several different available crystal growth technologies. The more rarefied wurtzite-type crystal structure facilitates doping when adjusting the phase-matching (PM) conditions.

Although the first LiInS_2 crystals appeared in the 70th, a high chemical activity of lithium and a considerable volatility of some components, resulting in considerable variation of composition and in turn of their chemical and physical properties prevented from growing bulk crystals of good quality. Only recently a technique for obtaining large crystals up to several cubic centimetres in volume was worked out and a detailed study of these crystals was continued³. The as grown LiInS_2 crystals were found to be colorless or slightly yellow while after annealing in sulfur vapour the samples became reddish. A special testing on thin samples gave identical band gap value for all samples independent of color: $E_g=3.72$ and 3.57 at 80 and 300 K, respectively³, while coloration is a result of point defects presence. The annealed samples demonstrated two dominating absorption bands at 480 nm (EIIb,c) and 540 nm (EIIa). An additional band at 740 nm (EIIa), which was found in some samples, did not affect the colour. An intense band at 360 nm in as grown LiInS_2 samples disappeared after annealing in sulfur and was related to sulfur vacancy, V_S . Chemical analysis showed that composition of all studied LiInS_2 crystals was close to a stoichiometric one although a lithium deficit and an indium excess was present. Thus a part of indium ions substitutes lithium and this antisite defect, In_{Li} , was supposed to be responsible for a broad absorption band at 380 nm and an intense blue photoluminescence which both are characteristic for all LiInS_2 samples studied³. In the present paper the identity of crystal structure in all LiInS_2 samples was confirmed using a single crystal X-ray diffraction analysis while the lattice parameters varied slightly. On the other hand the phase-matching conditions for second harmonic generation (SHG) were experimentally determined using a set of available laser systems and they were found to be similar for colourless and reddish samples, although there is a difference between them both and a theoretical curve built in accord with Boyd's data of 1973². Changes in colour were found to be much stronger in LiInSe_2 : in contrast to previous data⁴ the as grown LiInSe_2 samples were found to be yellow while after annealing in Se vapour their colour changes to dark red. Nevertheless combined X-ray diffraction study and optical spectroscopy showed that in LiInSe_2 these effects are also due to point defects.

2. EXPERIMENTAL DETAILS

2.1 Crystal growth

The bulk LiInS_2 and LiInSe_2 crystals were grown by the Bridgman-Stockbarger technique in vertical set-ups with counter-pressure on (001) and (010) seeds. The starting reagents were with 99,999% for S, Se and In, and 99.9% for Li nominal purity. Sulfur was additionally purified by sublimation in dynamic or static vacuum while metals were cleaned by repeated zonal melting and directed crystallization. Partial attention was paid to ratios between starting Li, In, S, Se elements. A correction of the stoichiometric $\text{Li:In:S(Se)}=1:1:2$ ratios was made taking into account different stability of the elements to weight loss during the runs because of volatilization and interaction between melt and container walls. To avoid Li interaction with silica ampoule a synthesis was performed in a special polished graphite crucible located inside silica ampoule. Some sulfur losses took place because of its interaction with graphite walls. An additional post-growth thermal treatment in S (Se) vapor at temperature close to melting point was made to remove the small opaque inclusions of different phases. Since vapor composition and partial pressure of gaseous species were unknown the optimized conditions for high quality crystal obtaining were empirically found. Using X-ray diffraction technique rectangular optical elements of certain orientation relative to crystallographic axes were cut from boules and their opposite working faces were polished for optical measurements.

2.2 X-ray diffraction study

The crystal structure determination for different LiInS_2 and LiInSe_2 samples was performed using CAD4 diffractometer along with the SHELXL97 structure determination/refinement program.

2.3 Optical spectroscopy

Optical transmission spectra were recorded in a whole transparency region using Shimadzu UV-3101 PC UV/VIS-NIR and Bomem FTIR spectrometer. For measurements in polarised light the film polarizers were used. A sample with parallel opposite faces was located inside metal vacuum cryostat, cooled by liquid nitrogen, which provided 90 to 600 K temperature variation.

2.4 Nonlinear experiments

Three different set-ups were used as IR sources of fundamental radiation for investigation of SHG process in LiInS_2 crystals:

- **IR source 1, which covers 1.8 to 2.6 μm spectral range.** The pump source is a LiNbO_3 nanosecond OPO pumped by a 15-ns pulsed Nd:YAG laser with 10 Hz repetition rate providing a typical output pulse energy of over 700mJ. This infrared OPO is continuously tunable from 1.8 to 2.6 μm , with a pulse duration $\tau = 10$ ns and a 100-mJ output (signal + idler) energy. After pump and signal rejections, a fraction of the idler beam, which varied from 0.5 to 5mJ was used as the fundamental wave for SHG. The beam profile at the crystal is a flat spot with diameter $2w = 3\text{mm}$. The idler wavelength λ ranges from 2.35 to 2.6 μm and has a full spectral width $\Delta\nu = 0.7$ nm, well below the quasi lambda non-critical spectral PM bandwidth ($\Delta\lambda \sim 49\text{nm}$). At the exit of the sample, the fundamental wave is reflected by a specific set of filters with a calibrated transmission at the harmonic. The uncoated sample is mounted on a computer-controlled motorized rotation stage which rotation axis has been set at 45° from the vertical to the table, in order to project the vertically polarized pump wave into two components (along Z and in the XY plane). The harmonic pulse energy is measured with a pyroelectric detector and the pump wavelength is determined (to $\pm 2\text{nm}$) by a scanning monochromator (2m focal length) and an InAs photodetector.
- **IR source 2 (2.8-12 μm).** A 1 kHz 800 nm, 800 μJ pulse from a Ti:sapphire laser was used to pump a parametric generator/ amplifier OPG/OPA system (TOPAS, Light conversion). The latter generated tunable signal (1.2-1.6 μm) and idler (1.6-2.1 μm) waves, which are then difference-frequency mixed in a AgGaS_2 crystal to give tunable infrared from 2.8-12 microns. The IR pulse duration is 250-300 fs and the spectral width is $50\text{--}70\text{ cm}^{-1}$. Typical pulse energies in the infrared are about 5-10 μJ .

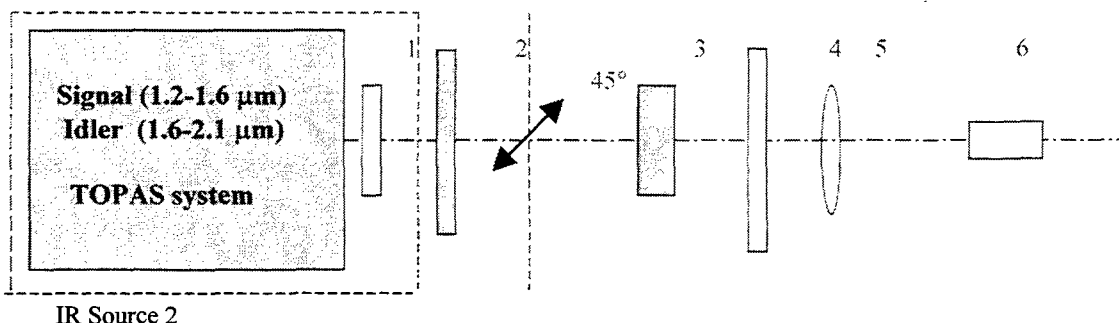


Fig.1 A scheme of nonlinear measurements with Ti-sapphire laser pumped OPG/OPA system as an IR source of fundamental radiation (Source 2). 1- an AgGaS_2 nonlinear element for mixing signal and idler components; 2- a long wave pass filter ($T > 2.5\text{ }\mu\text{m}$); 3- a LiInS_2 NLO element under investigation, rotated around horizontal axis; 4- a glass filter, separating a SH radiation; 5- a BaF_2 lens and 6- a MCT detector for SH radiation. An arrow shows fundamental wave polarisation for the II type PM case.

- **IR source 3 (4.5-40 μm):** A short-wavelength free-electron laser of the FELIX facility in Nieuwegein, the Netherlands. Pulse energies are around 10-20 μJ per pulse. The picosecond micropulses are grouped in a train of 5 μs duration (macropulse) with a micropulse spacing of 40 ns (or 1 ns). The macropulses are repeated at 10 Hz. The micropulse duration can be tuned from 200 fs to about 2 ps, while maintaining a fourier-transform limited spectrum.

2. RESULTS AND DISCUSSION

The as grown bulk crystals were up to 20 mm in diameter and 40 mm long for LiInS_2 and up to 10 mm, 20 mm, respectively, for LiInSe_2 . A preliminary testing using conoscopic techniques showed that all grown samples are single crystals. As grown LiInS_2 samples were colorless or yellowish while annealing changed their color to reddish. As grown LiInSe_2 crystals were yellow and annealing changed their color to dark red. Both changes in crystal structure and point defects can be responsible for color changes. In multicomponent compounds the phase diagram can be of very complicated structure and an area of homogeneity related to a certain phase is sometimes only about 1 w.% in width. In such case one can have another crystal structure after annealing in proper vapors and just this effect is used to remove the small inclusions inside bulk AgGaS_2 and AgGaSe_2 crystals. A nonlinear susceptibility is determined by the lattice structure and it is important to become sure that structure is the same in all crystals. Thus it is necessary to understand what is the origin of color changes in LiInS_2 and LiInSe_2 crystals. Four different structurally sensitive techniques were used:

1. An X-ray diffraction technique (Table 1);
2. The transmission spectra were recorded for especially performed plates about 0.1 mm thick, a form of fundamental absorption edge was analyzed and a band gap width, E_g , was measured; a longwave edge of the transparency region is also structurally sensitive since it is determined by specific vibrations in the lattice.
3. The attempts to change the color under proper illumination were made: in the case of point defects it is possible to change their charge state and thus to affect the color.
4. A second harmonic generation: the phase-matching conditions is a structurally sensitive parameter and it changes considerably at structure transformation.

Table 1 Lattice parameters for LiInS_2 and LiInSe_2 single crystals of different color

Formula	LiInS_2 (C1)	LiInS_2 (C2)	LiInS_2 (C3)	LiInSe_2	LiInSe_2	LiInSe_2
Color	Colorless	Yellowish	Rose	Yellow	Rose	Dark red
Space group	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$
$a, \text{\AA}$	6.8744(8)	6.8915(7)	6.8930(4)	7.1917(8)	7.1939(8)	7.1934(10)
$b, \text{\AA}$	8.0332(14)	8.0563(10)	8.0578(4)	8.4116(10)	8.4163(10)	8.4159(11)
$c, \text{\AA}$	6.4624(9)	6.4784(5)	6.4816(3)	6.7926(8)	6.7926(8)	6.7971(9)
$V, \text{\AA}^3$	356.88(9)	359.68(6)	360.00	410.90(8)	411.27(8)	411.49(9)

3.1 LiInS_2

Absorption spectra for LiInS_2 crystals for EIIa polarisation, in which all bands, mentioned in ref.^{3,4} appear, are given in Fig.2a. One can see the main bands at 480, 540 and 740 nm, which are responsible for variations in crystal color from colorless to rose³. All crystals studied have the same form of the fundamental absorption edge which can be described by a relation of the form $\alpha h\nu = A(h\nu - E_g)^{1/2}$. Such relation is valid for allowable direct transitions between the simple parabolic bands^{3,4}, the band gap values are $E_g = 3.72$ eV at 80 K and 3.57 eV at 300 K. Form and position of the longwave absorption edge are also identical. The X-ray data, obtained for all samples, give the same space group as $\text{Pna}2_1$ and the lattice parameters are similar (Table 1, first three columns). UV illumination was noticed to decrease a rose color of annealed LiInS_2 crystals, while He-Ne laser red radiation removed a grey color (photoinduced effects will be reported elsewhere). Thus, a complex of techniques shows that a color of different LiInS_2 samples is due not to structural difference but to variations in concentration and charge state of certain point defects in the crystal lattice.

The phase-matching properties of LiInS_2 have been studied earlier by Boyd *et al.*². They showed that the most efficient processes are type-II (eoe) phase-matched in the (a, b) plane, for which SHG occurs between the two angular noncritical wavelengths (along a -axis) of 2.32 μm and 5.88 μm . Using a one-pole Sellmeier equations fitted by Ch.Ebbers, we cut a 5x5x5 mm³ element at $\phi = 66.1^\circ$ in the $(X, Y) \equiv (b, a)$ plane. Note that, for standardization sake, our assignation for the crystallographic axes is $(XYZ) \equiv (bac)$ such that $n_x < n_y < n_z$, differing thus with the one used in ref [2], $(XYZ) \equiv (abc)$.

When the Kleinman symmetry conditions is assumed ($d_{32} = d_{24}$, $d_{31} = d_{15}$), the effective

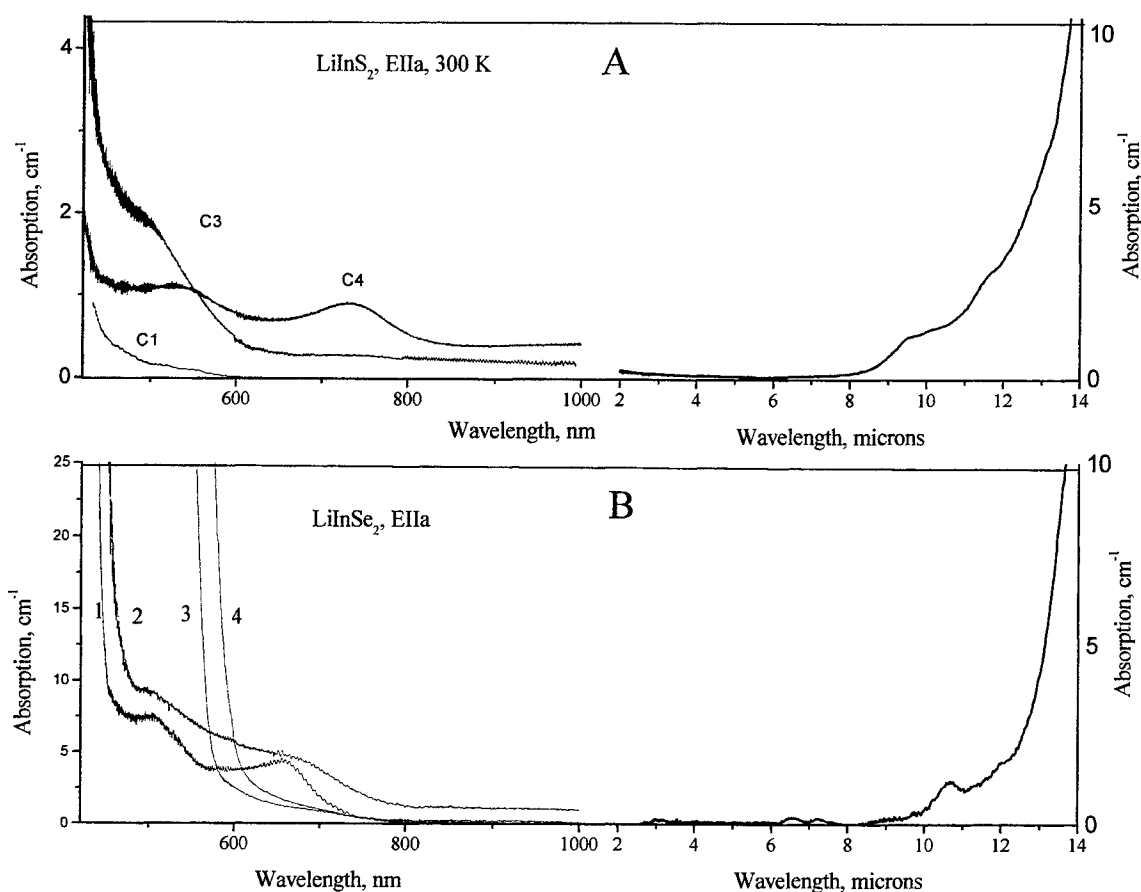


Fig.2 Absorption spectra for LiInS_2 (A) and LiInSe_2 (B) samples 1 mm thick. In Fig 2A C1 and C4 are LiInS_2 samples are colorless and gray-reddish as grown crystals, while C3 was annealed in sulfur vapor [3]. In Fig.B spectra 1,2 were obtained for yellow as grown LiInSe_2 and 3,4 correspond to dark red sample. Spectra 1,3 and 2,4 were recorded at 80 K and 300K, respectively. Spectra C3, C4 and 2 in Figures A and B, respectively are shifted upwards for clarity.

nonlinear coefficient for an (eoe) interaction in the XY plane is $d_{eff}^{II}(\varphi, \theta = 90^\circ) = d_{32} \sin^2 \varphi + d_{31} \cos^2 \varphi$. From the calibrated (using GaAs) wedge technique measurements at $10.6\mu\text{m}$ and $1.06\mu\text{m}$ (LiInS_2 cannot phase-match SHG for these wavelengths), Boyd *et al* found that d_{31} and d_{32} have the same sign with $d_{31} = 15 \text{ pm/V}$, $d_{32} = 9.7 \text{ pm/V}$, $d_{33} = 18 \text{ pm/V}$ (using $d_{14}(\text{GaAs}) = 134 \text{ pm/V}$ [2]). This would give $d_{eff}^{II} = 10.6 \text{ pm/V}$ for our SHG of $2.5 \mu\text{m}$.

Fig. 3 shows the dependence of the SH pulse energy as a function of the fundamental pulse energy, obtained in experiments with IR source 1 in 2.3 to $2.7 \mu\text{m}$ region. The Figure displays the expected quadratic dependence in the regime of low conversion efficiency (the maximum conversion $E(2\omega)/E(\omega)$ does not exceed 1%). From a fit to a quadratic law, one can deduce an energy conversion coefficient of $\Gamma = E(2\omega)/[E(\omega)]^2 = 2J^{-1}$. Assuming the same pulse duration at ω and 2ω the plane-wave conversion formula leads to a preliminary rough determination of $d_{eff} \approx 3.4 \text{ pm/V}$, about 3 times smaller than the expected value deduced from non-phase-matched SHG [3]. In Fig. 4, we show the recorded angular bandwidth of the phase-matching, as a function of the internal angle which yields $\Delta\varphi = (0.8 \pm 0.1)^\circ$ at a phase mismatch

$\Delta kL/2 = \pm 0.443\pi$ (FWHM). Superimposed to it we have plotted the plane-wave theoretical $\text{sinc}^2(\Delta kL/2)$ curve deduced from the indices of Boyd, which yields $\Delta\phi_B = 0.9^\circ$. The agreement is excellent for the crystal length (5 mm) used, which indicates a good crystal homogeneity over the whole volume⁵.

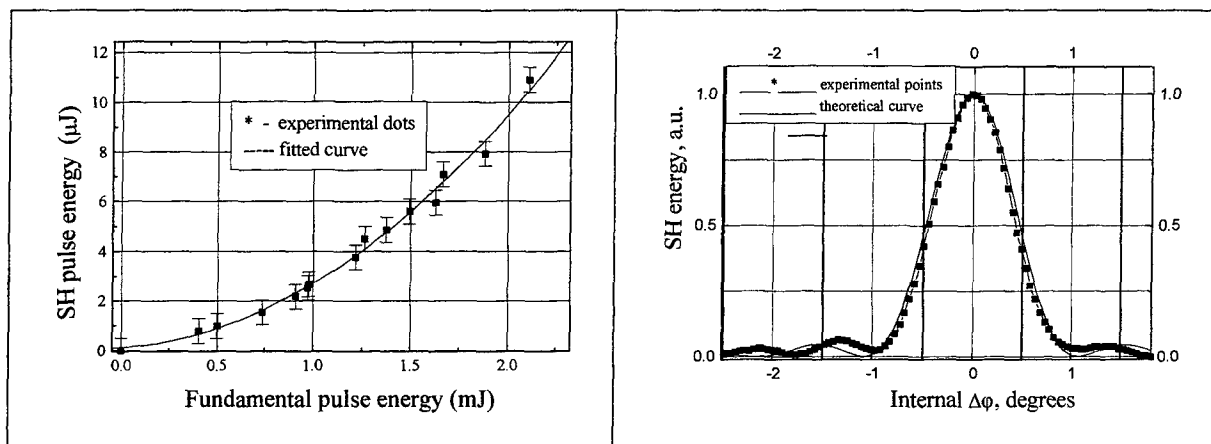


Fig.3 SH pulse energy corrected for blocking filters loss and Fresnel reflections loss on the crystal facets versus fundamental energy at $\lambda = (2841 \pm 2)\text{nm}$. The measured internal phase-matching angle is $\phi = 72.4^\circ$.

Fig.4 Internal angular acceptance bandwidth at nearly normal incidence at $\lambda = 2611\text{nm}$ ($\phi = 66.3^\circ$). The symbol curve is experimental data with $\Delta\phi = 0.8^\circ$ compared to the grey theoretical curve with $\Delta\phi = 0.9^\circ$ computed with ref.[2]. The sample size is $5 \times 5 \times 5\text{ mm}^3$.

The theoretical curve for phase-matching conditions was built using the refractive indices from² and fitting equation as $n^2 = A + B/(C + \lambda^2) + D\lambda^2$ with A, B, C, D, values from Table 2⁶. In Fig.5 the phase matching experimental data obtained using different IR sources 1 to 3 are compared with theoretical curve in a wide spectral region where the SH generation was predicted in ref². In the insert especially results for a shortwave region are given: one can see a good correlation in the form between theoretical and experimental curves although one can see an angle offset of $\sim 3^\circ$ (or a wavelength shift of $\sim 50\text{nm}$). A cross at $\lambda = 2.31\text{ }\mu\text{m}$ corresponds to noncritical phase matching (NPM) at $\Theta = 90^\circ$ and $\phi = 90^\circ$ (along Y or a axis), which was demonstrated by Ch.Ebbers in 1999⁶. At longer waves a good enough correlation between experimental PM curves for yellow, as grown and rose, annealed LiInS_2 samples although for them both an angle offset of ~ 3 to 5° from theoretical curve was found (Fig.5). One can infer that the Boyd's data give a good prediction on the birefringence value of LiInS_2 but need to be refined.

Table 2 Sellmeier parameters for LiInS_2 ⁶.

	α or Y	β or X	γ or Z or 2 fold axis
A	4.418222	4.559534	4.59206
B	0.1254461	0.1403701	0.1410887
C	-0.0657432	-0.69233	-0.069287
D	-0.0028850	-0.0028731	0.0030589

Optical damage threshold was measured using a free electron laser operating at 1 GHz with a beam focused to a Gaussian waist of $410\text{ }\mu\text{m}$ with an irradiated area of about $1.3 \times 10^{-2}\text{ cm}^2$. The macropulse energy is 14.5 mJ, so the fluence is about 1.1 J/cm^2 . The peak power in this case is 3.6 μJ per micropulse in 750 fs leading to 4.8 MW. Thus a peak intensity, corresponding to optical damage threshold of a rose, annealed LiInS_2 element, was estimated to be about $4.8\text{ MW}/1.3 \times 10^{-2}\text{ cm}^2 = 370\text{ MW/cm}^2$, while for a yellow sample it is about 20 % lower.

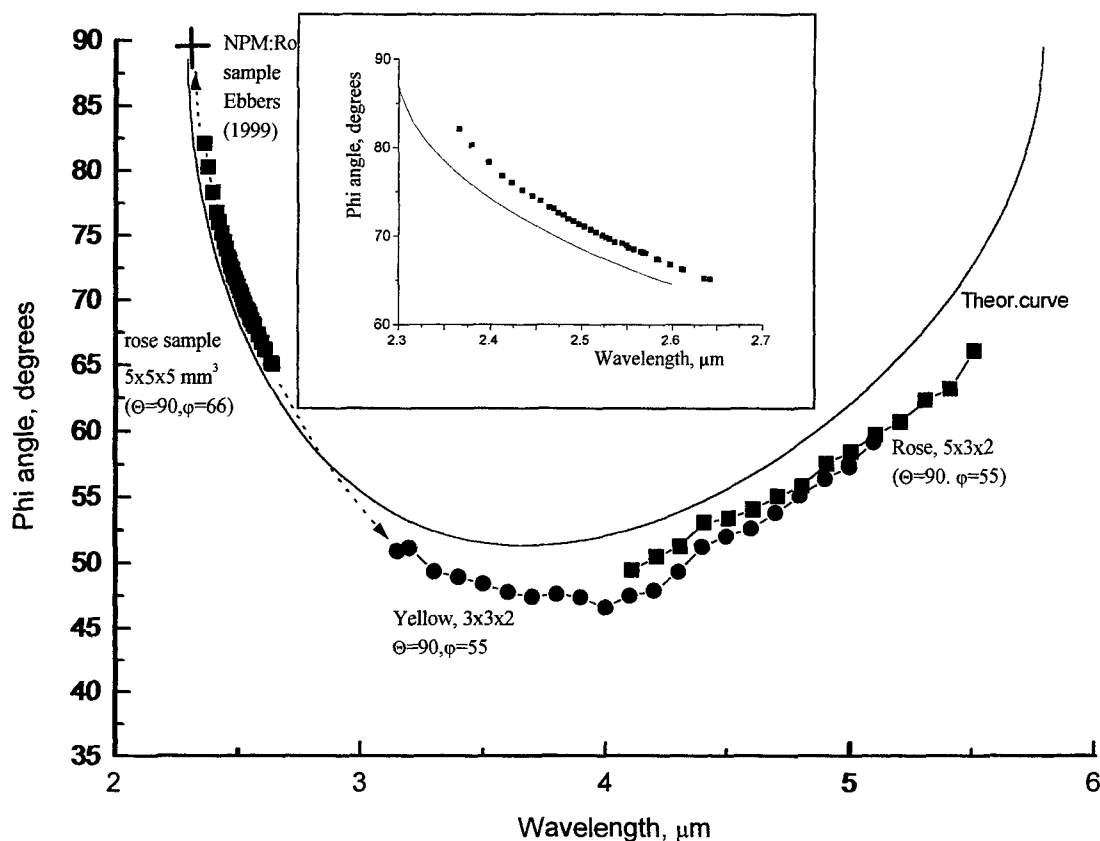


Fig. 5 Wavelength dependence of the internal phase-matching angles for different LiInSe_2 samples in comparison with a theoretical curve built basing on data from [2]:

at $2.31 \mu\text{m}$ and in 2.38 to $2.7 \mu\text{m}$ range – for a rose, annealed sample, $5 \times 5 \times 5 \text{ mm}^3$ in size;

in 3 to $5.0 \mu\text{m}$ range – for a yellow, as grown LiInSe_2 $3 \times 3 \times 2 \text{ mm}^3$ in size;

in 4.2 to $5.5 \mu\text{m}$ – also for a rose, annealed sample $5 \times 3 \times 2 \text{ mm}^3$ in size.

In the insert: data for a shortwave range represented in extended scale.

3.2 LiInSe_2

To date from previous luminescence, resistance, absorption and diffuse reflectance measurements the energy of the fundamental absorption edge of LiInSe_2 is not established reliably and falls into the range of 1.6 – 2.0 eV ⁷. Thus LiInSe_2 are expected to have a red color and nobody grew yellow bulk crystals. We studied carefully absorption spectra of LiInSe_2 samples, both as grown and annealed in selenium vapor. Absorption spectra for different in color LiInSe_2 crystals 1 mm thick are given in Fig.2B. One can see a sharp α decrease in the shortwave region : at $\sim 450 \text{ nm}$ and $\sim 590 \text{ nm}$ for yellow samples and dark red samples, respectively. Two additional broad absorption bands can be seen at 500 and 660 nm for yellow samples. When LiInSe_2 is heated from 80 K to room temperature the shortwave absorption edge, measured at 15 cm^{-1} level, is shifted 16 nm (0.096 eV) for yellow LiInSe_2 and $\sim 23 \text{ nm}$ (0.087 eV) for a dark red one. As the next step we decreased the crystal thickness to $d = 100 \mu\text{m}$. In contrast to LiInSe_2 ³ thin crystals had also different color: the annealed sample remained red. Indeed, in absorption spectra (Fig. 6) one can see a considerably different spectra again : only yellow crystals demonstrate a sharp fundamental absorption edge while for red samples the curves are more smooth and a well pronounced bend near 540 nm is present. Analysis of the form of absorption spectra shows that they can be approximated by a straight line when $(\alpha \cdot h\nu)^2$ is plotted versus photon energy $h\nu$ (Fig.7). As for LiInSe_2 this case corresponds to allowed direct transition between simple parabolic bands⁴ and band gap values E_g are 2.86 and 2.87 eV for EIIa and EIIb at 300 K , while at 80 K the same values are 3.01 and 3.04 eV . Illumination by a visible light with $\lambda \sim 400$ – 500 nm from 1 kW Xe lamp

through MDR2 diffraction monochromator was found to remove a red color of annealed LiInSe_2 crystals and to make them yellow. Thus it is obvious that a red color of LiInSe_2 crystals is due to some kind of point defects (maybe interstitial selenium Se_i). This conclusion is in a good agreement with X-ray data (Table 1) which show that all LiInSe_2 crystals studied have identical structure (space group $\text{Pna}2_1$, wurtzite-type lattice) as well as with the fact that a longwave edge of the transparency spectrum also does not depend on crystal color (dominating vibrations are the same in crystal studied).

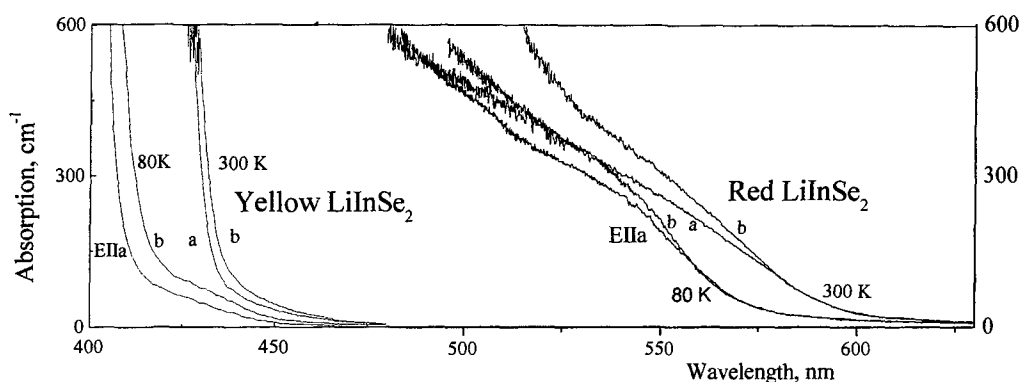


Fig. 6 Absorption spectra of LiInSe_2 plates 100 μm thick, cut from yellow and dark red samples. Spectra were recorded at 80 and 300 K for EIIa and EIIb polarizations.

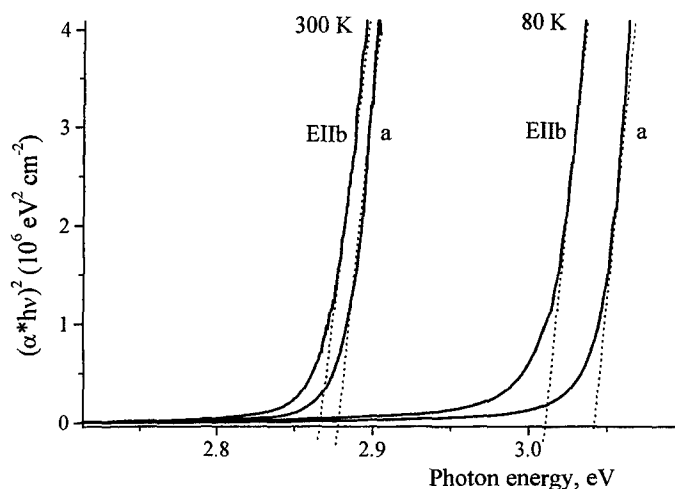


Fig. 7 Absorption spectra for yellow LiInSe_2 plate 100 μm thick, represented in $(\alpha^* \hbar \nu)^2 = f(\hbar \nu)$ coordinates.

The results of present report confirm that both yellow and dark red LiInSe_2 crystals have the same wurtzite-type structure and are suitable for nonlinear optics. The determined E_g values ~ 3 eV show that this crystal has the largest band gap among ternary selenium-containing compounds, indeed. To date the most important properties such as a nonlinear susceptibility and phase matching conditions are still unknown. In analogy with other compounds one can suppose that a nonlinear susceptibility is at least two times higher than that of its sulfur analogue, LiInS_2 . Determination of these parameters is of great importance and the work is in progress.

4. CONCLUSIONS

1. Bulk single crystals up to 20 mm in diameter and 40 mm long for LiInS_2 and up to 10 mm, 20 mm, respectively, for LiInSe_2 were obtained. Their color changed from colorless to rose for the first one and from yellow to dark red for the other. All crystals have a wurtzite-type lattice ($\text{Pna}2_1$ space group), lattice parameters were determined.
2. Color variations are due to point defects, first of all interstitial sulfur, resulting in additional wide absorption bands in the shortwave part of transparency range. For LiInS_2 the SHG phase matching conditions were found to be similar for samples of different color and some difference from Boyd's predictions of 1973 was shown: for XY plane $\Delta\phi \sim +3^\circ$ at $2.6 \mu\text{m}$ and $\Delta\phi \sim -3$ to -5° at $4\div 5 \mu\text{m}$. Nonlinear susceptibility for LiInS_2 was estimated: $d_{\text{eff}}(\text{XY}) \sim 3.4 \text{ pm/V}$ relative to Boyd's value as 10.6 pm/V . The optical damage threshold was estimated to be $\sim 350 \text{ MW/cm}^2$ for given regime.
3. Both yellow and dark red LiInSe_2 crystals have the same wurtzite-type structure. Difference in color is due to point defects and resulting intense absorption bands near the fundamental absorption edge. A proper illumination gives a photoinduced change of LiInSe_2 color from dark red to yellow as a result of changes in charge state of point defects. A band gap for LiInSe_2 was found to be 3.02 and 2.86 eV at 80 and 300K, respectively.

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